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Use of Genie 2000 and Excel VBA to correct for γ -ray interference in the determination of NORM building material activity concentrations

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Abstract

The γ -radiation emitted by building materials is calculated from the activity indices for ^{232}Th , ^{226}Ra and ^{40}K and expressed as the activity concentration index (ACI). Gamma spectroscopy is a non-destructive technique frequently used to simultaneously determine the indices for several radionuclides. Spectral interpretation poses a number of challenges, including identification of γ -lines subject to summing-in effects, interference from other γ -ray emitting radionuclides and the time required to reach secular equilibrium. These challenges are not fully addressed by Canberra Industries' Genie 2000, the software used by many laboratories to analyse samples. This article describes a Microsoft Excel workbook that exploits Genie 2000 flexibility to program applications with Visual Basic using Canberra's nuclear data access library and batch procedure tools. The workbook determines ^{40}K activity concentration after correcting for ^{228}Ac interference and ^{226}Ra activity directly from the γ -peak at 186.5 keV. The method proposed was tested by participating in 13 national and international scale inter-comparison exercises. The results were statistically indistinguishable from the reference values at a coverage factor of $k=3$ and no statistically significant differences were identified between the respective means by a Student's t pairwise comparison.

Keywords

Gamma-ray spectrometry; NORM; Spectral interferences; ^{40}K , ^{232}Th and ^{226}Ra activity concentration; Canberra Data Access Library; Genie 2000

1. Introduction

European Directive 2013/59 (EURATOM Directive) (EU, 2013) is the Union's most recent legislation on safety standards for the prevention of exposure to ionising radiation. Its Article 75 provides that 'the reference level applying to indoor external exposure to the gamma radiation emitted by building materials, in addition to outdoor external exposure, shall be less than 1 mSv γ^{-1} (Xhixha et al., 2017). That reference level applies to existing standard products as well as recycled waste containing naturally occurring radioactive materials (NORMs). The Directive established a screening tool (Activity Concentration Index, ACI) for identifying materials that may cause that this mentioned reference level is exceeded when they are used as building material (Puertas et al., 2015). The ACI is calculated from the following expression:

$$ACI = \frac{C_{^{226}\text{Ra}}}{300} + \frac{C_{^{232}\text{Th}}}{200} + \frac{C_{^{40}\text{K}}}{3000} \quad (1)$$

where $C_{^{226}\text{Ra}}$, $C_{^{232}\text{Th}}$ and $C_{^{40}\text{K}}$ are the activity concentrations in $\text{Bq}\cdot\text{kg}^{-1}$ for radium (equivalent to uranium under secular equilibrium conditions), thorium and potassium, respectively.

Very low detection limits are not required in building materials such as concrete, cement, brick and aggregates, since the mean worldwide concentrations are 50 $\text{Bq}\cdot\text{kg}^{-1}$ for ^{226}Ra , 50 $\text{Bq}\cdot\text{kg}^{-1}$ for ^{232}Th and 500 $\text{Bq}\cdot\text{kg}^{-1}$ for ^{40}K (Janković and Todorović, 2011). Radioactivity is normally evaluated with γ -ray spectrometry, a non-destructive technique that can simultaneously perform multi-nuclide determinations. Based on the detection of photon emissions, it requires no sophisticated sample treatment but it does require careful calibration of the γ -detectors with suitable samples (Daza et al., 2001) or Monte Carlo methods (Laborie et al., 2002). The first step in the procedure is to ascertain whether the activity concentration of a given γ -ray emitting radionuclide can be found directly or whether it must be determined indirectly by measuring the γ -lines of its progeny at secular equilibrium. In either case the right γ -lines must be chosen to correct (or otherwise) for possible interference and take care of γ -lines subject to significant summing-in effects (García-Talavera et al., 2001). A number of challenges must therefore be addressed when determining ^{226}Ra , ^{232}Th and ^{40}K activity concentrations: coincidence summing, interference and the storage times required to reach secular equilibrium.

Canberra Industries' Genie 2000 software, one of the packages most commonly used in gamma spectrometry, provides a platform for γ -detector data acquisition and analyses the resulting spectra with advanced algorithms. Genie 2000 records all the information analysed in an *.CAM file and laboratory analysis is routinely conducted to a user-defined step-by-step procedure that can be saved to an *.ASF file for ready repetition. Such analysis is limited to linear instruction sequences that involve no iteration (loop) or conditional (if, else) structures. Canberra Industries has developed DataAccess, a component written in Visual Basic that defines all CAM file data storage and retrieval properties and methods. In addition, the system's batch procedures provide for more flexible Genie 2000 routines than the step-by-step

approach. The Genie 2000 data access component and batch procedures can be linked to Microsoft Excel via Microsoft's Component Object Model (COM) (Forgács et al., 2014). Genie 2000 features a calculation tool, '*NIDw Interference correction*', that corrects for possible interference in the gamma ray emissions on a sample spectrum, based on the activity concentrations calculated, line by line, for each gamma emission possibly present in the sample. The alternative method proposed by the authors consists in correcting the γ -peak counts prior to determining the activity concentration. Of the two procedures for determining peak count, deconvolution (detector resolution permitting) or using other photopeaks for the same radionuclide or others in secular equilibrium with it, the latter was deployed here, for it is easier to apply when performing routine analyses on a large number of samples.

The working hypothesis defended in this study is based on the preceding considerations. It contends that sample measurements taken immediately, i.e., without waiting to reach secular equilibrium, can deliver sufficiently precise and accurate results if ACI is determined from the ^{226}Ra γ -peak at 186.5 keV, corrected for ^{235}U interferences, and from the ^{40}K γ -peak at 1460 keV, corrected for ^{228}Ac interference, and care is taken to avoid the use of lines affected by coincidence summing as far as possible. The advantage of not having to wait for secular equilibrium between ^{222}Rn and its progeny is that no correction is needed for the possible loss of ^{222}Rn from the sample container. Here, moreover, gamma ray attenuation for low energy photons was excluded given the equivalence between the apparent densities of the calibration sources and the samples. The objectives pursued in this study include selecting the most suitable γ -peaks, implementing a code developed in Visual Basic to provide interoperability between Microsoft Excel applications and Genie 2000 and verifying the reproducibility of the concentration activity values obtained with the proposed code in inter-comparison exercises using 13 samples with different matrices.

Materials and methods

2.1. Laboratory description and detectors

The Spanish CIEMAT (Energy, Environment and Technology Research Centre) Environmental Radioactivity and Radiological Surveillance (UR and VR) Department's γ -spectrometry laboratory has nine high purity germanium detectors (one standard coaxial, two broad energy coaxial, three extended range coaxial and three reverse electrode coaxial HPGe) with relative efficiencies of 25.0 % to 115.7 %. HPGe detector resolution ranges from 1.72 keV to 2.05 keV for the ^{60}Co peak at 1.33 MeV. The detectors are protected either by 150 mm iron shielding or lead shielding lined with copper or tin to absorb the fluorescent X-rays emitted by the lead. The aforementioned shields also effectively block natural terrestrial radiation. The detectors are connected to five racks consisting in 9 HV power supply units, 9 spectroscopy amplifiers and 9 Canberra Industries ADCs. Spectra are saved to the computer memory with five Canberra Industries acquisition interface modules (AIMs) and analysed with standard Canberra Industries Genie 2000 software. The detectors are located in the basement of a 50-year-old building in a continuously ventilated, air-conditioned room kept at a constant 21 °C.

Laboratory radon concentration ranges from 5 Bq·m³ to 134 Bq·m³ with a mean of 35 Bq·m³. The background of all detectors is measured every six months at a count time of 600,000 s.

2.2. CAM File

Genie 2000 software is one of the most commonly used tools in γ -spectrometry. In addition to its utility in step-by-step analysis of γ -spectra (CANBERRA, 2012), Genie 2000 accommodates algorithms written in Visual Basic (CANBERRA, 2009a). To further facilitate analysis, the routines can be executed using its batch procedures tool (CANBERRA, 2009b). Spectra acquired and analysed are stored in a CAM file (extension *.CNF) generated by the software (Figure 1). CAM files contain two types of data: parametric and spectral (32-bit integer arrays). Parametric data, single numbers or text strings accessed by means of symbolic code, are grouped into 'classes', labelled acquisition, sample, geometry, processing, peak search results, nuclide identification, display, certificate, calibration results, analysis control, quality control or miscellaneous. Three levels of parametric data can be identified: (1) individual, (2) record and (3) record tabular entry. Record parameters are sets of data referring to the same entity (such as data on a specific peak in the spectrum). This data items can be addressed individually by the parameter name or by the number of the item in the sequence. However, record parameters that can be grouped into higher level records (such as nuclides, the activity in their photopeaks or the minimum detectable activity for the nuclide in a given photopeak) are labelled 'tabular entry parameters'. All the parametric data used in this study are accessed via the code developed.

Fig. 1. CAM file diagram.

2.3 Determination of ^{226}Ra activity

^{226}Ra activity concentration can be determined on a γ -spectrum either directly by measuring the 186 keV γ -peak or indirectly by measuring the γ -peaks of its ^{214}Pb and ^{214}Bi progeny.

- a) Direct approach: measurement of the γ -peak at 186 keV

Where the former approach is adopted, the 185.72 keV (52 %) emissions from ^{235}U must be taken into consideration. Two procedures are possible: deconvolution (Zhang et al., 2009) or subtracting the ^{235}U contribution from the ^{226}Ra 186 keV peak. The uranium contribution can be determined by one of two methods.

- i) From sufficiently intense ^{235}U γ -peaks, i.e., at 205.3 keV (4.7%), 143.7 keV (10.5%) and 163.3 keV (4.7%) (Janković and Todorović, 2011). The 163.3 keV and 205.3 keV γ -peaks are subject to significant summing-incoincidences, due to the cascades at 19.6 keV-143.7 keV and 19.6 keV-185.7 keV and also these γ -peaks suffer from summing-out effects (García-Talavera et al., 2001). The 143.7 keV peak, in turn, is affected by interference from γ -ray emission at 144.2 keV by daughter ^{223}Ra (Dowdall et al., 2004), whilst ^{228}Ac emissions at 204.0 keV (0.11%) interfere with the 205.3 keV peak (Baumgartner et al., 2017). In light of the foregoing and the low activity concentration of ^{235}U in building materials, this method is of scant utility.
- ii) From ^{238}U activity concentration as determined with its daughter ^{234}Th and granddaughter $^{234\text{m}}\text{Pa}$ nuclides when secular equilibrium is reached after 160 d (Mubarakmand et al., 1977), given that in the vast majority of soils ^{234}Th and $^{234\text{m}}\text{Pa}$ are in equilibrium with their parent. As γ -spectrometry is a non-destructive technique that entails no radiochemical analysis, the likelihood that ^{234}Th and $^{234\text{m}}\text{Pa}$ are in equilibrium with ^{238}U is high (Lau et al., 1982). Consequently, the 63.3 keV or 92.6 keV (92.4 + 92.8 keV doublet) γ -peaks from ^{234}Th (Coursol et al., 1990) or the 766.4 keV or 1001.0 keV peaks from $^{234\text{m}}\text{Pa}$ (García-Talavera, 2003) can be used. The weak intensity of $^{234\text{m}}\text{Pa}$ γ -peaks, in conjunction with the low efficiency of germanium detectors at higher energies, often leads to non-detectable count rates for building materials (García-Talavera, 2003). Furthermore, $^{234\text{m}}\text{Pa}$ γ -emission at 766.36 keV (0.323 %) interferes with the γ -peak generated at 768 keV (4.76 %) by ^{214}Bi (Yücel et al., 1998). Inasmuch as the 92.6 keV doublet is also a thorium α_1 X-ray peak, in samples with a high thorium content, this γ -peak fails to provide an accurate indication of uranium activity concentration because thorium α_1 X-rays would self-excite (Lau et al., 1982). The 63.3 keV γ -peak (3.75 %) contains 63.9 keV emissions (0.235 %) from ^{232}Th , 62.9 keV emissions (0.0164 %) from ^{231}Th and 62.9 keV emissions (0.0164 %) from ^{234}Th (Joshi, 1987). Of the three, only the emissions from ^{232}Th constitute potential interference (Papachristodoulou et al., 2003).

Given the low activity of ^{235}U in most building materials, the use of ^{238}U to determine the activity of ^{235}U is reasonable, for the activity ratio for this nuclide is constant in all environmental samples, except where contaminated by processed uranium or taken from

certain specific, well-known locations. The $^{238}\text{U}/^{235}\text{U}$ activity ratio is 21.71 ± 0.03 (Dowdall et al., 2004).

b) Indirect approach: measurement of the γ -peaks generated by the radon progeny

As radon is a noble gas, the use of ^{222}Rn progeny to determine ^{226}Ra entails several drawbacks.

- i) It calls for equilibrium between ^{226}Ra and its progeny, which normally requires a suitably long storage period (≥ 20 d) (Scholten et al., 2013).
- ii) As a result of radon diffusion across the container holding the sample, ^{226}Ra activity may be underestimated by an unknown factor (Arafa, 2002; Zhang et al., 2009). Moreover, if the container has a screw-on lid with a fairly coarse thread or a non-air-tight lid, radon may diffuse through small gaps between the bottle and the lid, inducing a 15 % to 20 % error in the readings (Mauring and Gäfvert, 2013). That development alters the secular equilibrium between ^{226}Ra and its progeny, prompting potentially significant errors in the activity calculations.
- iii) So-called recoil emanation and diffusion emanation render the distribution of radioactivity non-uniform, even though the sample was ground to a very fine particle size. Recoil emanation occurs when some of the ^{222}Rn (from decaying daughters of ^{226}Ra) settle on the surface of solid grains. Diffusion emanation is the capacity of ^{222}Rn to migrate across interstitial space in the sample. These two effects depend on moisture content, temperature, porosity, grain size and barometric pressure (Benke and Kearfott, 2000). Radon as an inert gas may also accumulate at the top of the container, depending on whether there is a void between the sample and the lid. In either case, short-lived radon decay products (^{214}Bi and ^{214}Pb) are generated not only in the matrix but at the top of the sample. The result is that the source and sample geometry differ, reducing efficiency by 5 % where 100 % of the volume is occupied and by 20 % where the container is 70 % filled.

In light of the foregoing considerations, the method chosen here to determine ^{226}Ra was to suppress the ^{235}U contribution to the γ -peak (based on the 63.3 keV γ -line for ^{234}Th) at 186.5 keV (as in a) ii) above).

2.4. Determination of ^{232}Th activity

As ^{232}Th emits no γ -rays, equilibrium among ^{232}Th , ^{228}Ra and ^{228}Ac can be assumed in most building materials and ^{232}Th activity concentration can therefore be determined from the emissions of its decay daughters ^{228}Ac , ^{212}Pb and ^{208}Tl . Although with a half-life of 55.6 s ^{220}Rn exhibits lower diffusion across the sample particles than ^{222}Rn , its measuring geometry count efficiency still varies, albeit much less widely. Further to the working hypothesis defined to the effect that gamma emitters need not be in secular equilibrium to be used, ^{232}Th activity can be determined from the γ -rays emitted by its daughter, ^{228}Ac , rather than waiting the 4 days it takes to reach secular equilibrium between ^{220}Rn and its progeny. Several intense ^{228}Ac γ -lines have been described at 338.4 keV, 911.1 keV and 968.9 keV (Murray et al., 1987). The γ -ray at 338.32 keV (11.4 %) receives interference from ^{223}Ra emissions at 338.28 keV (2.85 %)

(Živanović et al., 2012). The ^{228}Ac γ -lines at 965 keV and 969 keV overlap partially and although the peak at 969 keV is identified in all background measurements, its area depends on the identification of the peak at 965 keV. As this peak may be interpreted to form part of the continuous background that generates a count deficit around the peak at 969 keV, the count rates in these peaks have been deemed unreliable (Korun et al., 2012). Despite the single summing-in and the 14 summing-out effects present in the γ -peak at 911.1 keV (see Table S1.1), the likelihood of emission is low. The impact on the total γ -peak count consequently lies within the range of measuring uncertainty, inasmuch as the samples (building materials) exhibit low environmental activity values. On those grounds, ^{232}Th was determined here from the 911.1 keV γ -rays emitted by ^{228}Ac .

2.5. Determination of ^{40}K activity

Whilst most authors determine ^{40}K activity concentration from its γ -line at 1460.8 keV, only a few papers describe the interference induced by ^{228}Ac emissions at 1459.13 keV (0.87 %) (Lavi et al., 2004). Where that contribution is not taken into consideration, the systematic influence for ^{40}K (ϵ_K) is:

$$\epsilon_K = 9.3 \cdot \left(\frac{K}{Th} \right) \quad (2)$$

where K is activity concentration for ^{40}K in Bq kg^{-1} , Th the activity concentration for ^{232}Th in Bq kg^{-1} and 9.3 percentage error calculated by the authors cited. In light of this error, expressed in percentage, ^{40}K activity concentration is determined from its γ -line at 1460.8 keV after correcting for ^{228}Ac interference.

2.6. Interference correction

Peak count rate is the information that the algorithm proposed must transfer to Genie 2000 to calculate ^{226}Ra and ^{40}K activity concentration. For ^{226}Ra the 186 keV count rate is found from:

$$C(186) = C(^{235}\text{U}, 185.7) + C(^{226}\text{Ra}, 186.21) \quad (3)$$

where $C(^A\text{X}, E_\gamma)$ is the count rate for a γ -ray with energy E_γ emitted by nuclide ^AX . The count rate for ^{235}U is found from ^{234}Th emissions at 63.3 keV as:

$$C(^{235}\text{U}, 185.7) = f^{-1} \cdot \frac{\epsilon(185.7) \cdot q(^{235}\text{U}, 185.7)}{\epsilon(63.3) \cdot q(^{234}\text{Th}, 63.3)} \cdot C(^{234}\text{Th}, 63.3) \quad (4)$$

where $q(^A\text{X}, E_\gamma)$ and $\epsilon(E_\gamma)$ are the emission probability and detection efficiency for the E_γ keV γ -ray and f is the activity ratio between ^{238}U and ^{235}U . The count rate for the 63 keV peak is:

$$C(63) = C(^{234}\text{Th}, 63.3) + C(^{232}\text{Th}, 63.9) \quad (5)$$

The count rate for ^{232}Th is found from the ^{228}Ac emissions at 911.1 keV as:

$$C(^{232}\text{Th}, 63.9) = \frac{\varepsilon(63.9) \cdot q(^{232}\text{Th}, 63.9)}{\varepsilon(911.1) \cdot q(^{228}\text{Ac}, 911.1)} \cdot C(^{228}\text{Ac}, 911.1) \quad (6)$$

For ^{40}K the 1460 keV count rate is found from:

$$C(1460) = C(^{40}\text{K}, 1460.1) + C(^{228}\text{Ac}, 1459.13) \quad (7)$$

The count rate for ^{228}Ac is found from the ^{228}Ac emissions at 911 keV as:

$$C(^{228}\text{Ac}, 1459.13) = \frac{\varepsilon(1459.13) \cdot q(^{228}\text{Ac}, 1459.13)}{\varepsilon(911.1) \cdot q(^{228}\text{Ac}, 911.1)} \cdot C(^{228}\text{Ac}, 911.1) \quad (8)$$

2.6. Uncertainty estimation

Corrected count rate uncertainty is found with the Kragten method (Kragten, 1994; Kragten, 1995), which is readily programmed because it is applicable to any manner of mathematical expression and it can be easily implemented in code (see Appendix S2). Moreover, as the method is designed for a spreadsheet, it can be converted into a matrix containing the respective cells.

3. Program structure and code features

Although the Excel worksheet containing the code can be used without running Genie 2000, the application is assumed to be resident in the computer. Figure 2 shows a screenshot of the worksheet. Users can download the Excel file from this [link](#) and make amendments at will to meet their needs. The code developed in Visual Basic for MS Excel Workbook applications is reproduced in Appendix S2.

Four files are required to run the code: the file containing the spectrum (extension *.CNF), the background file (extension *.CNF), the calibration file (extension *.CAL); and the library file (extension *.NLB). The file pathways are read by clicking on the 'Run' button, which calls up the VBA command 'Application.GetOpenFilename'.

3.1. Analysis sequence

As noted earlier, Genie 2000 batch procedures provide for more flexible analysis. All the executable files are located in the "EXEFILES/" directory. The analysis sequence is executed by clicking the 'Run' button, which calls up the 'AnalysisSequence' procedure (see Appendix S2). Sequence analysis is performed on the user-selected spectrum file as follows.

1. Peak identification. Performed by the executable file 'PEAK_DIF.EXE', which uses Mariscotti's (1967) well-known second difference peak-finding algorithm. The significance threshold is set at 3.0.
2. Net peak area. Calculated by least-squares non-linear regression performed by the file 'AREA_ML1.EXE'. The arguments included in the program are as follows: number of

channels on each side of the peak; energy tolerance (2.0 keV); fitting for singlets and non-linear least squares fitting for multiplets (threshold=6.0 and minimum separation from neighbours=1.0 keV). In this case study, the number of channels on each side of the peak was varied to maximise activity concentration accuracy determined with the function 'BackgroundChannelsFinder' (Appendix S2).

3. Correction for area. Performed by subtracting the user-selected background file ('AREACOR.EXE').
4. Correction for peak interference (described in section 3.2). Subject to confirmation of satisfactory sample spectrum efficiency by the 'CopyEff' procedure, which uses the Canberra Nuclear Data Access Library's 'CopyBlock' method. This method copies all the calibration data contained in calibration spectrum class CAM_CLS_GEOM.
5. Efficiency correction. Found for the user-selected calibration file with the dual polynomial efficiency calibration equation (EFFCOR.EXE).
6. Nuclide identification and activity concentration calculation (NID_INTF.EXE). The arguments are transferred to the executable file with energy tolerance set at 2.0 keV and the NID confidence threshold at 0.8 for acceptance or rejection of identification of candidate peaks. The NID confidence threshold is a confidence value used to accept or reject candidate peaks for identification; this value has a range of 0 (low) to 1 (high).
7. Minimum activity concentration. Determined to Currie criteria (Currie, 1968) (MDA.EXE). Nuclides and their activities are entered on the spreadsheet by running the 'FinalResults' procedure described in section 3.5.

All the executable files are run with the procedure 'ExecCommand', which calls up the Windows 'OpenProcess' API.

Fig. 2. Screenshot of a representative worksheet.

3.2. Peak interference suppression

Peak interference is suppressed as in expressions (4), (6) and (8). The program opens the spectrum file as follows (see Appendix S2).

1. 'DataAccess' is defined using the Canberra Nuclear Data Access Library.
2. 'Open method' is invoked by transferring a string comprising the pathname of the measured spectrum.
3. Peak parameters are obtained from the 'CAM_CLS_PEAK' class, which contains the record parameters:
 - a) peak energy ('CAM_F_PSENERGY'),
 - b) peak area ('CAM_F_PSAREA'),
 - c) peak area uncertainty ('CAM_F_PSDAREA')
 - d) counts per second ('CAM_PSCTSS')
 - e) counts per second uncertainty ('CAM_F_PSCERR').

Record parameter information is read from the spectrum file as follows.

1. The number of records in the class is obtained with the property 'NumberofRecords'.
2. Record parameters are set to a given variant vector with the property 'ParamArrayEx'. The variant vector is used here because Visual Basic automatically changes the types of variables entered.
3. The following arguments must be transferred to this property: record parameter name, number of records and procedure for raising the number of records.
4. A loop is used to iterate the variant vector elements.

The interference corrected count rates and their uncertainties are assigned to record parameters 'CAM_F_PSCTSS' and 'CAM_F_PSCERR' as described in sections 2.5 and 2.6. That does not alter subsequent spectrum functionality, inasmuch as all other parameters remain intact. Moreover, only record parameters 'CAM_F_PSCTSS' and 'CAM_F_PSCERR' are used by Genie 2000 to calculate sample activity and uncertainty.

3.3. Efficiency and associated uncertainty

Efficiency and the associated uncertainty are requisite to determining the counts corrected with expressions (4), (6) and (8).

Efficiency for a given range of energy is found with the 'EffToEnergy' function (see Appendix S2). This function uses the fitting parameters for the efficiency calibration equation, grouping the low energy parameters under 'CAM_F_DLALFACx' (with $1 \leq x \leq 6$) and the high energy parameters under 'CAM_F_CHALFACy' (with $1 \leq y \leq 10$). One or the other set is used depending on the value of the crossover parameter, which defines the intersection between the quadratic equation to which the low energy levels are fitted and the polynomial equation to which the high energy values are fitted. If the energy entered in the function to perform the calculations

is lower than the crossover point, the 'CAM_F_DLCALFACx' parameters are used, and if it is higher, the 'CAM_F_CHCALFACy' parameters are applied. When the fit is performed without a crossover point, i.e., when parameter 'CAM_F_CROSSOVER' is 0, the 'CAM_F_DHCALFACy' parameters are used.

Efficiency uncertainty is computed with the 'uEfficiency' function (see Appendix S2), which reads two tabular entry parameters, 'CAM_F_DEFF' and 'CAM_F_DEFFERR' from the spectrum file. The tabular entry parameter 'CAM_F_DEFF' contains the experimental efficiency values obtained with efficiency calibration and 'CAM_F_DEFFERR' the uncertainties associated with such values. The procedure for reading this tabular entry parameter is as follows:

1. The number of records in the class is obtained with the property 'NumberOfRecords'.
2. The number of entries in the record is obtained with the property 'NumberOfEntries'.
3. Parameters are set to a given variant vector with the property 'ParamArrayEx'. The following arguments must be transferred to this property: record parameter name, number of records, the procedure for raising the number of records, 'iRec'=0 and 'iEntry'=0.
4. A loop is used to fill the variant vector elements.

Absolute efficiency uncertainty necessary for computing the uncertainty of the corrected counts is calculated with the Bambyneck criterion from the expression:

$$u^2 (ef) = \left(\sum_{i=1}^n \text{CAM_F_DEFFERR}_i^{-2} \right)^{-1} \quad (9)$$

where CAM_F_DEFFERR_i is the uncertainty associated with the i -th of the n efficiency values on the efficiency calibration curve for the detector. This uncertainty only takes into account the individual uncertainty of each efficiency of the calibration curve and not that due to fitting which it will be considered by Genie 2000 in the activity concentration calculation.

3.4. Corrected count uncertainty

As noted in section 2.6, uncertainty is determined with the Kragten method. The function used, 'UncertaintyCalculator' (Appendix S2), has four-arguments: a string contained in the equation from which uncertainty is estimated and three variant vectors. One vector contains the equation symbols and the other two the respective values and associated uncertainties. The text string is converted into a mathematical function using the 'VBScript' library's 'Eval' method. A loop fills in the matrix needed to apply the Kragten method.

3.5. Activity concentration, uncertainty and detection limit findings

The activity concentration findings, associated uncertainties and sample detection limits are entered on the Excel spreadsheet by the 'FinalResult' procedure, reading the following record

parameters that are subsequently listed on the spreadsheet: 'CAM_T_NCLNAME' (radionuclide name), 'CAM_G_NCLWTMEAN' (activity concentration value), 'CAM_G_NCLWTMERR' (activity concentration uncertainty) and 'CAM_G_NCLMDA' (detection limit).

4. Results and discussion

The activity concentrations found for ^{232}Th , ^{226}Ra , ^{40}K and ^{214}Pb in 15 samples analysed in 13 inter-comparison exercises organised by the Institut de Radioprotection et de Sûreté Nucléaire (ISRN), the International Atomic Energy Agency (IAEA), the Consejo de Seguridad Nuclear (CSN), TUD COST Action TU 1301 NORM for Building Materials (NORM4BUILDING) and Metrology for Processing Materials with High Natural Radioactivity (METRONORM) from 2009 to 2017 are given in Table 1 and Figures 3 to 5. As ^{232}Th was not included in the exercises, the results assessed are for ^{232}Th and ^{228}Ac . ^{228}Ac activity concentration, in turn, is required both per se and to correct for its interference in ^{40}K activity concentration.

Figure 3 shows that the laboratory activity concentrations found for ^{228}Ac were lower in most cases than the inter-comparison reference values. As noted in section 2.4, the γ -peak areas and hence activity concentration were lower than expected because of the many summing-out effects in the ^{228}Ac γ -peak at 911.1 keV. As the likelihood of summing-out emissions was <1 % in 86 % of cases, however (see section 2.4) they would lie within the range of count uncertainty. Although the activity concentration for this radionuclide, divided by a factor of only 200 (Equation 1), carries the greatest weight in the ACI, it was only 6.6 % lower on average than the reference values and with the exception of one outlier all the values overlapped by 38 % at coverage factors of $k=1$ and $k=2$ and 15 % at $k=3$. The outlier was included in the table, inasmuch as its inclusion corrected for the ^{40}K and ^{234}Th interferences with which the ^{235}U counts used to determine ^{226}Ra activity were calculated.

The variation in the number of channels on the two sides of the peak used to calculate the area was studied for ^{226}Ra (Quittner, 1969). The optimal number of channels was determined from the minimum χ^2 value in the Gaussian fit for the ^{234}Th peak at 63 keV. Of the three peaks used to calculate ^{226}Ra activity concentration, the one at 63 keV was chosen because it exhibited the largest error, an approach deemed more expedient than attempting to calculate the spectrum baseline, which involved greater complexity. The baseline for the peaks at 186 keV and 911 keV, also used in the calculations, were more linear, however. The χ^2 value was taken from the 'CAM_F_PSFIT' parameter. The same χ^2 criterion was used to calculate the areas for ^{40}K and ^{228}Ac and their activity concentrations. No pattern was observed in the graph plotting the activity concentration values found against the reference values (Figure 4), whilst an 85 % overlap was observed for coverage factor $k=1$ and 15 % for $k=2$ (Table 1). The mean deviation from the reference values was 2.4 %.

^{40}K activity concentration was 5.6 % lower on average than the reference values. Given that the background variation due to ^{40}K was more stable than the variation due to the ^{222}Rn progeny, the background used would logically be higher than expected, resulting in lower activity concentration (Figure 5). Even with that deviation, however, overlap was acceptable,

as 40 % of the values overlapped at coverage factors of $k=1$ and $k=2$ and 20 % at $k=3$. Those findings, along with the fact that the activity concentration for this radionuclide was divided by 3000, attested to the scant significance of this deviation for ACI calculations. Nonetheless, further study would be needed to narrow the divergence observed.

Figure 3. Activity concentrations for ²³²Th/²²⁸Ac in 13 inter-comparison exercises

Figure 4. Activity concentrations for ²²⁶Ra in 13 inter-comparison exercises

Figure 5. Activity concentrations for ^{40}K in 13 inter-comparison exercises

Conclusions

The Excel workbook designed fulfils the primary purpose of this study, for it delivers ^{226}Ra activity concentration with no need to wait for the nuclide to reach secular equilibrium with its progeny, as well as ^{40}K activity concentration net of ^{228}Ac interference. The workbook can be used by any laboratory that analyses γ -ray spectra with Genie 2000 software. Nonetheless, the method is only applicable to samples containing natural uranium.

The photopeaks used to determine the ACI were selected minimising possible coincidence summing and avoiding and correcting for spectral interferences from other gamma emitters.

When used in 13 national and international scale inter-comparison exercises and applying a coverage factor of $k=3$, the procedure yielded statistically undistinguishable results. Negative deviations relative to the reference values were nonetheless observed for ^{228}Ac due to summing out effects and for ^{40}K due to the background suppression procedure applied. These issues will be studied in greater depth in future research to further enhance the accuracy of the method proposed.

The prospects for this line of study include enlarging on the functionality of the Excel workbook to address direct calculation of the ACI with its associated uncertainty; and calculation of the detection threshold further to standard ISO 11929 for cases such as studied here in which the photopeaks exhibit interference.

Table 1. Activity concentrations for $^{232}\text{Th}/^{228}\text{Ac}$, ^{226}Ra and ^{40}K in 13 inter-comparison exercises.

Proficiency test	Matrix	Year	Units	$^{232}\text{Th}/^{228}\text{Ac}$			^{226}Ra			^{40}K		
				Reference activity	Laboratory activity	Overlap	Reference activity	Laboratory activity	Overlap	Reference activity	Laboratory activity	Overlap
ISRN - 96 SL 300	Sediment	2009	Bq kg ⁻¹	101.870 ± 0.028	100.69 ± 0.91	k=2	160.0 ± 60	17.12 ± 57	k=1			
IAEA-CU-2009-03	Moss	2009	Bq kg ⁻¹	37.0 ± 1	36.8 ± 6.7	k=1	26.0 ± 2.0	29.3 ± 7.5	k=1	55.0 ± 2.0	52.0 ± 14.1	k=1
CSN-2010	Food ash	2010	Bq kg ⁻¹	5.26 ± 0.24	3.9 ± 1.1	k=2	15.2 ± 1.4	13.8 ± 4.8	k=1	45.93 ± 4.1	45.09 ± 13.12	k=1
IAEA-TEL-2011-04	Soil	2011	Bq kg ⁻¹	41.0 ± 1.0	20.6 ± 4.0	NO	50.2 ± 2.0	50 ± 12	k=1	48.5 ± 1.1	47.3 ± 12.7	k=1
CSN-2012	Soil	2012	Bq kg ⁻¹	17.4 ± 0.8	15.24 ± 0.37	k=2	27.0 ± 2.5	32.0 ± 1.2	k=2	26.6 ± 2.4	23.5 ± 4.2	k=2
IAEA-410	Sediment	2013	Bq kg ⁻¹	8.40 ± 0.30 (*)	6.78 ± 0.66	k=2	194.0 ± 9.5	23.19 ± 9.5	k=2	11.6 ± 2.5	10.6 ± 5.2	k=2
IAEA-412	Sediment	2013	Bq kg ⁻¹	36.6 ± 0.55 (*)	33.2 ± 1.1	k=3	27.10 ± 5.2	27.2 ± 4.2	k=1	56.0 ± 1.1	49.4 ± 12	k=3
IAEA-TEL-2014-04	Water-1	2014	Bq kg ⁻¹				14.210 ± 60	16.3 ± 1.1	k=1			
	Water-2	2014	Bq kg ⁻¹				37.5 ± 3.2	39.4 ± 6	k=1			
	Sediment	2014	Bq kg ⁻¹	12.1 ± 0.75	10.55 ± 0.45	k=2	19.0 ± 4.8	16.5 ± 3	k=1	27.0 ± 2.7	26.5 ± 5.8	k=1
CSN-2014	Plant ash	2014	Bq kg ⁻¹	19.2 ± 1.2	14.2 ± 1.2	k=3	27.9 ± 2.4	28.3 ± 7.2	k=1	31.63 ± 6.0	36.71 ± 91	k=3
NORM4-Building (TU1301)	Fired clay	2015	Bq kg ⁻¹	61.0 ± 3.0	59.8 ± 1.0	k=1	125 ± 11	12.43 ± 4	k=1	95.5 ± 4.0	82.0 ± 34	k=2
MetroNorm (IND57-REG3)	Water	2015	Bq L ⁻¹	6.01 ± 0.32	6.07 ± 0.19	k=1	3.70 ± 0.5	3.08 ± 0.18	k=1			
CSN-2016	Soil	2016	Bq kg ⁻¹	32.2 ± 0.85	31.32 ± 0.77	k=1	32.9 ± 1.9	35.2 ± 3.0	k=1	36.1 ± 1.1	32.5 ± 7.3	k=2
IAEA-TEL-2017-04	Carbonate	2017	Bq kg ⁻¹	90.0 ± 2.0	87.7 ± 2.6	k=1	697.0 ± 20.0	69.06 ± 27.3	k=1			

(*) The reference value shown is for ^{232}Th .

Uncertainties are quoted for k=1.

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Supporting Information

Additional Supporting Information may be found in the online version of this article:

Appendix S1 – Summary of summing-in and summing-out effects for ^{228}Ac .

Appendix S2 – Visual Basic code for Microsoft Excel applications developed in this study.

The authors are solely responsible for the content of these materials. Queries may be directed to the corresponding author; requests for additional materials will be handled discretionally.

Highlights

- The measuring time needed for gamma subtraction is a challenge in environmental laboratories when there is a large number of samples to analyze.
- A Visual Basic code was implemented to generate a background spectrum by summing several background spectra.
- The generated spectrum with this alternative method is compatible with the analysis software.

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